

Polymerization of Vinyl Monomers Initiated by Thianthrene Cation Radical with Potential Biological Activity

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Abstract

Polymerization of vinyl monomers is promoted by thianthrene cation radical as a part of our research concerning the reactions of various agents with readily isolable, yet highly reactive species and elucidate the biological activity. Thianthrene cation radical initiated the homopolymerization and copolymerization of styrene and ethyl vinyl ether. The polymerization yields decreased as the concentration of phenylacetylene or diphenylethylene increased. Such polymereization by cationic thianthrene radical could provide some clues for the reaction in living animals. Comments on possible polymerization mechanisms were suggested.

Key words : Thianthrene, Cation Radical, Polymerization, Oxidation

1. Introduction

Cation radical chemistry has attracted great attention due to its main role in various important organic reactions.¹ Nonetheless, little is known for the reactions with alkenes and alkynes although organic cation radicals are known to react with a wide variety of nucleophiles.¹¹ The addition of cation radical such as R_2NH^+ and t -BuOH⁺ to alkenes is known.¹² However, polymerization of alkenes promoted by addition of a cation radical is not a common reaction.¹¹

The cationic polymerization of vinyl and heterocyclic derivatives, which usually proceeds via cationic chain carriers, can be initiated using various agents including Lewis and Bronsted acids, oxonium salts and using ionizing radiation.¹³ The persistent carbocation radical-initiated polymerization was first reported.^{14a} There are some examples of the use of carbocation radicals as an initiator of polymerization.¹⁴ By comparison, polymerization of vinyl derivatives initiated by the cation radical of thianthrene, a heteroaromatic cycle containing two

sulfur atoms in the *para* position, has not been reported. While carbocation radical crystals are synthesized by anodic electrocrystallization with difficulty or *in situ* generated,¹⁴ thianthrene cation radical perchlorate crystals with moderate storage life can be easily prepared.^{15,61} Thus, the reactivity study of thianthrene cation radical toward various nucleophiles including amines, aromatics, ketones, alkenes, alkynes, organometallic complexes, oximes, etc. has been much done.⁵ Thianthrene cation radical is reported to just form an adduct with alkenes and alkynes without polymerizing these unsaturated species (Scheme 1).¹⁵¹ The thianthrene cation radical with two sulfur atoms may display different modes of reaction from the heteroatom free carbocation radicals. Thianthrene is easily oxidized *in vivo* and *in vitro* to monosulfoxide or disulfoxide without cleavage of the ring structure.¹⁶ Therefore, such oxidation of thianthrene could induce some unidentified side reaction in living animals. Here we report our results on the polymerization of vinyl monomers promoted by thianthrene cation radical.

2. Experimental

2.1. Materials

Chemicals were purchased from Aldrich Chemical Co.. Methyl methacrylate and styrene were washed with

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aqueous 5% sodium hydroxide (to remove inhibitor), washed well with distilled water, dried over anhydrous MgSO_4 , and distilled at reduced pressure prior to use. Acrylonitrile was washed with dilute sulfuric acid, washed with aqueous sodium carbonate, dried over anhydrous MgSO_4 , and distilled before use. Phenylacetylene and 4-vinylpyridine were distilled at reduced pressure before use. Ethyl vinyl ether was distilled before use. Adduct of thianthrene cation radical to phenylacetylene^[5] and thianthrene cation radical perchlorate^[7] were prepared according to the literature procedure. The cation radical is saved at low temperature in the dark.

2.2. Instrumentation

All reactions and manipulations were performed under prepurified nitrogen atmosphere using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. All glasswares were flamed-dried or oven-dried before use. Infrared spectra were obtained using Perkin-Elmer 1600 Series FT-IR FT-IR spectrometer. Proton NMR spectra were recorded on a Varian Gemini 300 spectrophotometer using $\text{CDCl}_3/\text{CHCl}_3$ as a reference at 7.24 ppm downfield from TMS. Number average molecular weights (M_n) were determined by vapor pressure osmometry (VPO) in HPLC-grade chloroform using a Wescan Model 233100 osmometer and/or ^1H NMR spectroscopy.

2.3. Polymerization of styrene with thianthrene cation radical perchlorate

To a purple solution of thianthrene cation radical perchlorate (56.8 mg, 0.18 mmol) in methylene chloride (5 mL) cooled to 0°C was added styrene (2.06 mL, 18.0 mmol) under a stream of nitrogen. The reaction mixture turned brown within 5 min, and the reaction medium became then rapidly viscous with some exothermicity. After stirring at room temperature for 24 h, the polymer was precipitated in methanol, filtered off, and dried to yield 1.58 g (87%) of off-white powder. IR (KBr pellet, cm^{-1}): 3050 m, 2900 s(vC-H), 1600 m, 1495 m, 1450 s, 1020 w, 730 s, 670 s. ^1H NMR (δ , CDCl_3 , 300 MHz): 0.8-2.0 (br, 3H, CHCH_2), 6.2-7.4 (br, 5H, ArH). $M_n = 2850$ (measured by VPO).

2.4. Polymerization of ethyl vinyl ether with thianthrene cation radical perchlorate

To a solution of thianthrene cation radical perchlorate

(56.8 mg, 0.18 mmol) in methylene chloride (5 mL) at 0°C was charged ethyl vinyl ether (1.72 mL, 18.0 mmol) under a stream of nitrogen. The reaction mixture immediately turned dark brown, and the reaction medium became very rapidly viscous with exothermicity. The same workups yielded 1.10 g (85%) of light yellow powder. IR (KBr pellet, cm^{-1}): 2950 s(vC-H), 1375 m (vC-H), 1100 s (vC-O). ^1H NMR (δ , CDCl_3 , 300 MHz): 1.18 (br, 3H, OCH_2CH_3), 1.61 (br, 2H, backbone CH_2), 1.82 (br, 1H, backbone CH), 3.47 (br, 2H, OCH_2CH_3). $M_n = 1880$.

2.5. Copolymerization of styrene and ethyl vinyl ether with thianthrene cation radical perchlorate

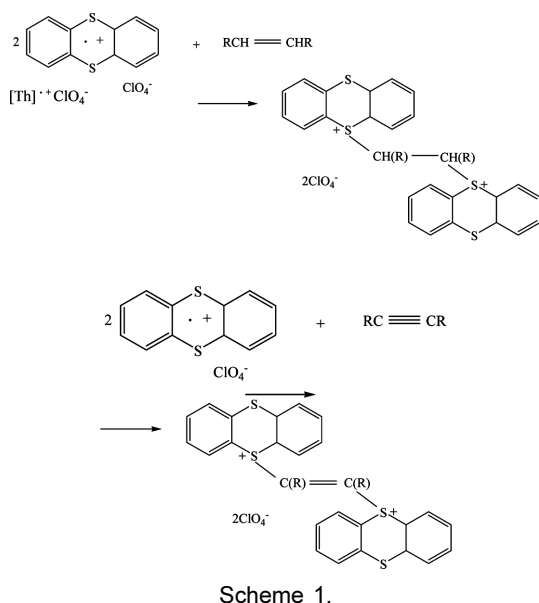
To a purple solution of thianthrene cation radical perchlorate (56.8 mg, 0.18 mmol) in methylene chloride (5 mL) at 0°C was added ethyl vinyl ether (0.86 mL, 9.0 mmol) and styrene (1.03 mL, 9.0 mmol) under a stream of nitrogen. The same workups gave 1.31 g (85%) of pale yellow powder. IR (KBr pellet, cm^{-1}): 3050 s, 2960 s(vC-H), 1807 m, 1716 m, 1600 m, 1445 m, 1450 s, 1375 m (vC-H), 1100 s (nC-O), 700 s, 500 s. ^1H NMR (δ , CDCl_3 , 300 MHz): 0.8-3.7 (br, all aliphatic CHn), 6.5-7.6 (br, ArH). $M_n = 2200$.

3. Results and Discussion

Thianthrene cation radical perchlorate which is a little shock-sensitive is a very reactive species yet having moderate storage life and can react with many agents in a number of ways.^[5] Thianthrene cation radical is reported to add to alkenes and alkynes without polymerizing them (Scheme 1).^[5] The polymerization yields drastically decreased with increasing molar ratio, [phenylacetylene] over [thianthrene cation radical perchlorate]: 87% for 0, 55% for 0.01, and 2% for 0.1 probably due to the adduct formation as shown in Scheme 1. The adduct of thianthrene cation radical to phenylacetylene could not polymerize styrene and ethyl vinyl ether. Thianthrene cation radical was found to initiate the ring-opening polymerization of THF with heating for 5 days at 50°C to produce oligo(THF) with $M_n = 793$ (by ^1H NMR spectroscopy) in 14% yield.

The molecular weight data of the polymerization reactions were summarized in Table 1.

Three mechanisms are possible for the initiation step: (A) bond-formation, (B) electron-transfer, and (C) HX-



Scheme 1.

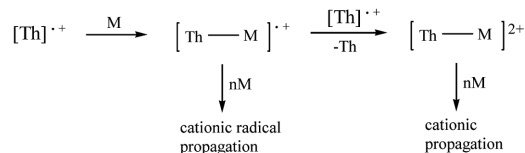
Table 1. Number average molecular weight data of polymerization of vinyl monomers promoted by thianthrene cation radical^a

Monomer	Yield (%)	Mol wt ^b
Styrene	87	2850
Styrene ^c	85	2820
Styrene ^d	55	2690
Ethyl vinyl ether	85	1880
Styrene + Ethyl vinyl ether ^e	85	2200

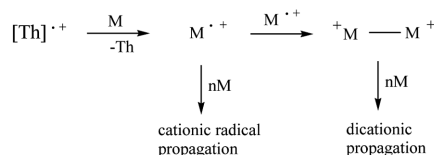
^aMonomer, 18 mmol; initiator, 0.18 mmol; methylene chloride, 5 mL for 24 hrs. ^bMeasure with VPO in chloroform. ^c Performed in the dark. ^d Phenylacetylene (0.18 mmol) added. ^e 1:1 molar ratio.

generation (Scheme 2). Among them the bond-formation mechanism can be first ruled out for the following reasons. The thianthrene cation radical initiated less effectively in the presence of phenylacetylene. The adduct of thianthrene cation radical to phenylacetylene did not polymerize styrene and ethyl vinyl ether. Furthermore, the thianthrene moiety was found not to be bound to the polystyrene and poly(ethyl vinyl ether) although the chains free of bound thianthrene moiety can be generated by the order unknown side reaction during the workup. The two remaining mechanisms would equally operate. The monomer cation radicals generated by the electron-transfer from thianthrene cation radical to monomers would initiate the polymeriza-

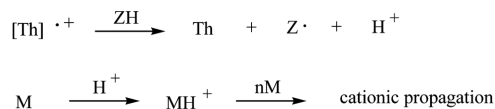
(A) Bond-formation initiation



(B) Electron-transfer initiation



(C) HX-generation initiation



Scheme 2.

tion reaction.

The monomer dication generated by combining monomer cation radicals would also initiate the polymerization reaction. Besides, thianthrene cation radical is a highly reactive species and can react in a number of ways.^[1] Generally, it will react with a nucleophilic species (ZH) with hydrogen to generate a Bronsted acid, HX, which can initiate the polymerization reactions.^[8] The propagation may proceed via cation radicals, cations, or dications, but simple propagation through free radicals seems unlikely due to facile oxidation by cation radicals.^[9] More than a single mechanism may be operating simultaneously, giving rise to a very complex situation. The polymers with low molecular weights may be produced by some unidentified side reactions, which could be related to the cationic nature of the initiator, in the complex situation. Study on the polymerization mechanism are currently in progress.

4. Conclusions

Polymerization of vinyl monomers is initiated by thianthrene cation radical as a part of our research concerning the reactions of various agents with readily isolable, yet highly reactive species and elucidate the biological activity. Thianthrene cation radical initiated

the polymerization of styrene and ethyl vinyl ether. The number average molecular weight of the polymers were in the range of 1800-2900. The polymerization yields decreased as the concentration of phenylacetylene or diphenylethylene increased. Such polymereization by cationic thianthrene radical could provide some clues for the reaction in living animals. Comments on possible polymerization mechanisms were provided.

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